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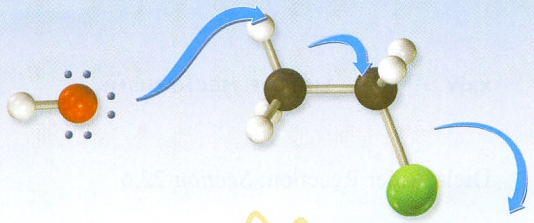

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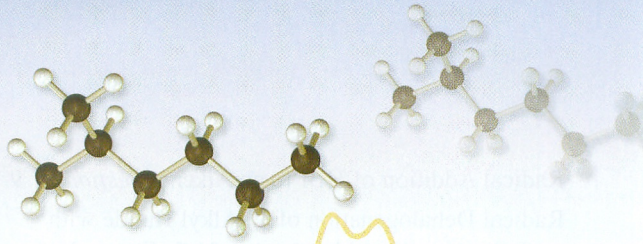
Unimolecular Nucleophilic Substitution (S_N1): *Section 8.6; Figures 8.6, 8.8, and 8.9*

Wolff-Kishner Reduction: *Section 18.8; Figure 18.4*



Preface

This book is intended for use in the first organic chemistry course taken by students majoring in chemistry, biochemistry, biological sciences, and other health-related fields. The unique organization of this book sets it apart from many other texts in this area; specifically, this text is organized according to the mechanisms of the presented organic reactions rather than according to functional groups. It covers all of the same material usually found in a book using the functional group approach but in an order based on mechanistic themes.

The organic chemistry course is a pivotal class taken by science students. In addition to the inherent importance of organic reactions in chemistry and biology, organic chemistry introduces and develops a type of reasoning and logic that is new to many students. A solid understanding of this subject is often critical to subsequent success in a science career.

Organic chemistry often has a reputation among students as being a very difficult course, involving an enormous amount of memorization. For students who approach the course by attempting to memorize all of the important information, it is a daunting subject indeed. The goals of this text are to help students be successful in organizing this vast amount of material, to stimulate their interest by making organic chemistry understandable and relevant, to demonstrate the logic and beauty of the field, and to provide a method to remember all of those many reactions.

Using an organization based on reaction mechanisms rather than the approach based on functional groups has always appealed to me. I believe that the mechanism approach encourages students to develop an understanding of why things occur rather than just memorizing what occurs. In writing this book, my goal throughout has been to present organic chemistry in a way that is clear, understandable, and accessible to students. *Mechanisms are used as the organizing principle that helps students learn organic chemical behavior, not as the major concept to be learned.* Unlike a graduate-level or advanced undergraduate book, this text is not intended to be an encyclopedia of mechanisms. Those mechanisms that are general and that organize a number of reactions are emphasized, whereas those that are uncommon are often not covered at all.

Changes in This Edition

Organization

The first three chapters constitute a review of bonding and an introduction to organic compounds. Functional groups are introduced. Resonance is covered extensively, and numerous examples are provided. Acid–base chemistry is discussed in Chapter 4, and this reaction is used to introduce many of the general features of reactions, including the effect of structure on reactivity. Nomenclature of all of the functional groups is covered in Chapters 5 and 12. In this edition, stereochemistry is covered in two chapters to break up the material: Chapter 6 discusses cis–trans isomers and conformations, and Chapter 7 addresses chiral molecules.

Chapter 8 begins the treatment of organic reactions with a discussion of nucleophilic substitution reactions. Elimination reactions are treated separately in Chapter 9 to make each chapter more manageable. Chapter 10 discusses synthetic uses of substitution and elimination reactions and introduces retrosynthetic analysis. Although this chapter contains many reactions, students have learned to identify the electrophile, leaving group, and nucleophile or base from Chapters 8 and 9, so they do not have to rely as much on memorization. Chapter 11 covers electrophilic additions to alkenes and alkynes. The behavior of carbocations, presented in Chapter 8, is very useful here. An additional section on synthesis has been added to this chapter as well.

IR spectroscopy is covered in Chapter 13, and hydrogen and carbon NMR spectroscopy are covered in Chapter 14. These topics have been separated to provide a more reasonable chapter size and to increase flexibility in order of presentation. Mass spectrometry and UV-visible spectroscopy are covered in Chapter 15, so these topics can be made optional if desired.

Aromatic chemistry is discussed earlier in this edition: Chapter 16 covers aromaticity, and Chapter 17 presents aromatic substitution reactions. Chapters 18 and 19 discuss additions to and substitutions at the carbonyl group. To keep these chapters from being overwhelming, aldol and ester condensations are covered separately in Chapter 20, which deals with reactions of enolate and related nucleophiles. Chapter 21 presents the chemistry of radicals.

All chapters have been designed to be as self-contained as possible, allowing the possibility of presenting them in a different order. For example, it is possible to cover the spectroscopy chapters earlier or later than they are presented in the text. As a further example, those wishing to present carbonyl chemistry earlier can cover Chapters 18, 19, and 20 immediately after Chapter 12.

Chapters 1 through 21 cover the topics that most instructors will include in their courses, with the possible exception of Chapter 15. The remaining chapters offer a choice for the last part of the course. They include chapters on pericyclic reactions, synthesis, and polymers. The chapters on the more biochemical topics—carbohydrates, amino acids and proteins, nucleotides and nucleic acids, and other natural products—concentrate on the organic chemistry of these important biomolecules.

Spectroscopy

Chapters 13 and 14 provide complete coverage of IR and NMR spectroscopy, respectively, and UV-visible spectroscopy and mass spectrometry are discussed in Chapter 15. These chapters can be covered earlier or later in the course as the instructor desires

without affecting other chapters. Numerous sample spectra and problems are included, and all spectra have been redrawn for increased clarity. Because all the functional groups have been introduced early, the spectroscopy of all of them is presented at one time. It is not necessary to return to a discussion of spectra each time a new functional group is introduced. Chapters after Chapter 15 have several spectroscopy-based problems in a separate section of the additional problems.

Synthesis

The use of reactions to synthesize organic compounds is introduced early and is an important part of every chapter in which reactions are presented. The first introduction to synthesis occurs in Chapter 8, with problems such as "What reagent and solvent would you use to carry out the following transformation?" and "Show how these compounds could be prepared from alkyl halides." Chapter 10 introduces the concept of synthetic equivalent (acetate for hydroxide and phthalimide for ammonia). Section 10.15 covers the strategy of organic synthesis and introduces retrosynthetic analysis; here the synthesis problems become more complex. A new section on synthesis in Chapter 11 introduces the retrosynthetic arrow and again raises the level of the problems. This process continues through the remaining reaction chapters. Chapter 23, a unique chapter on synthesis, brings together most of the reactions presented in earlier chapters; provides additional discussion of synthetic strategy and the use of protecting groups; and presents some longer, more complex syntheses. Table 23.1 lists the important carbon–carbon bond-forming reactions, and Table 23.2 lists most of the reactions presented in the book according to the functional group that is produced. These tables are very useful in designing syntheses and can also be used as a summary of most of the text.

ORGANIC Chemistry Now™

Introducing Organic ChemistryNow

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This completely new website is designed to engage students by helping them prepare for examinations. Organic ChemistryNow is an assessment-centered learning tool developed in concert with the approach and pedagogy in the text. Students take a pretest that includes questions that have been authored to reflect the level and approaches discussed in the text. They are then given a personalized learning plan based on their pretest results. The unique personalized learning plan directly links students to Molecular Model Problems, Mechanisms in Motion (animations of organic mechanisms), Coached Tutorial Problems, Building Block Review Problems, and Active Figures.

Key Features

- A brand **new design** has made the book visually appealing and pedagogically easier to read. In addition, color is used to highlight parts of molecules and to follow the course of reactions.
- **Up-to-date information** about reactions, reagents, and mechanisms has been added throughout.
- All **mechanisms** have been examined carefully for inclusion of all steps with arrow pushing, proper reagents, and conditions. Each mechanism is clearly labeled and easily identified by a tan background, and steps are numbered and annotated.

- Each chapter begins with a set of **Mastery Goals.** At the end of the chapter these goals are restated and linked to specific problems so that students can test their command of the material. In addition, **Mastery Goal Quizzes** for each chapter can be found on the website at Organic ChemistryNow.
- More than 1100 problems are included in this book, many with multiple parts. Many new **Practice Problems,** with in-text solutions, have also been added. Many of these include a **Strategy** section to guide students through the thought process involved.
- **Integrated Practice Problems** have been added at the end of many chapters to tie together ideas from the chapter and to demonstrate a process that can be used to decide which reaction in that chapter is occurring.
- Plentiful **problems** appear at the end of each chapter. These problems range from drill to challenging and include applications to the biological sciences, molecular models, and problems using spectroscopy.
- Because Organic Chemistry is a very visual science, considerable effort has gone into the development of chemical **illustrations** to make them both clear and informative. Most figures contain text as well as structures. This decreases the need to refer back and forth between the figure and the text.
- Extensive use of **molecular models,** both in-text and online, helps students visualize the shapes of compounds and how the molecules interact in three dimensions. In addition, **Model-Building Problems** are interspersed throughout the text to give students practice building handheld models. End-of-chapter problems based on online models are also included.
- Students can also assess their understanding of each chapter's topics with additional quizzing, conceptual-based problems, and tutorials at the **OrganicChemistryNow**™ website (see following for details).
- **Electrostatic potential maps** have been added throughout the text to illustrate the important concepts of electrophilicity, nucleophilicity, and resonance.
- The application of organic chemistry to **biological chemistry** is emphasized within the text, in the *Focus On Biological Chemistry* boxes, and within problems designated with the BioLink icon.

- **Focus On and Focus On Biological Chemistry** boxes illustrate applications of organic chemistry to the world around us and to the health sciences, explore topics in more depth, or discuss the history of chemical discoveries. Some topics include *DDT-Resistant Insects, Biological Alkylations and Poisons,* and *Environmentally Friendly Chemistry (Green Chemistry).*
- Animations of key concepts are found on **Organic ChemistryNow** as *Active Figures.* Taken straight from the text, *Active Figures* help students visualize key concepts from the book. The *Active Figures* also include questions so that students can assess their understanding of the concepts.
- Unique to this book are **Tables 23.2 and 23.3** on pages 1031–1043, which summarize the important carbon–carbon bond-forming reactions and most of the reactions presented in the text. Students can use these tables as an aid in designing the synthesis of more complicated problems.

- All definitions of key terms are collected in a **glossary** at the end of the text. Each glossary listing is keyed to the section of the text where the term is introduced.
- To improve the **layout and the flow** of the text and to emphasize applications of organic chemistry within the text, this edition has less boxed material. However, if you still wish to use some of the Elaboration boxes from the first edition, that material is available online at **Organic ChemistryNow.**

Support Package

For the Student

- **Student Study Guide,** by Joseph Hornback. This manual contains detailed solutions to all text problems. 0-534-39710-7
- **Pushing Electrons: A Guide for Students of Organic Chemistry,** third edition, by Daniel P. Weeks, Northwestern University. This paperback workbook is designed to help students learn techniques of electron pushing. Its programmed approach emphasizes repetition and active participation. 0-03-020693-6

- **Organic ChemistryNow** at **http://www.brookscole.com/hornback2,** developed by Paul R. Young (University of Illinois, Chicago). This web-based assessment-centered learning tool for the Organic Chemistry course was created in concert with this text. Throughout each chapter, icons with captions alert students to media resources that enhance problem-solving skills and improve conceptual understanding. In Organic ChemistryNow, students are provided with a Personalized Learning Plan—based on a diagnostic pretest—that targets their study needs and helps them visualize, organize, practice, and master the material in the text. PIN code access to Organic ChemistryNow is included with every new copy of the text.
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